

III. "Researches on the Arsenic-Bases." By A. W. HOFMANN, LL.D., F.R.S. Received November 24, 1860.

In a previous note* I have shown the existence of a group of diatomic bases, containing phosphorus and arsenic, which are formed by the action of monarsines on the bromethylated bromide, so frequently mentioned in my researches on the phosphorus-bases. The idea naturally suggested itself to examine the deportment of this salt under the influence of monostibines, with the view of producing the phospho-stibonium-compounds. The two bodies react upon one another, but only after protracted digestion or exposure to rather high temperatures. The product of the reaction is complex, yielding a comparatively small quantity of a difficultly soluble platinum-salt of diatomic appearance. I have repeatedly modified the circumstances and analysed the products in the form of platinum-salts; I omit to quote the detail of these experiments, since they have failed to disentangle the difficulties of the reaction.

Some experiments upon the deportment of dibromide of ethylene with triethylarsine were more successful. The reaction between these two bodies had been selected as a subject of inquiry by Mr. W. Valentin, to whom I am indebted for valuable assistance at the earlier stage of these researches. Circumstances have subsequently prevented Mr. Valentin from carrying out his plan, and I have therefore to take upon myself the responsibility for the following statements.

Action of Dibromide of Ethylene upon Triethylarsine.

MONARSONIUM SERIES.

The experience gathered during the examination of the phosphorus-bodies, enabled me to establish the nature of this reaction by a comparatively small number of platinum-determinations.

Bromide of Bromethyl-triethylarsonium.—To avoid as far as possible the formation of the second product, a mixture of triethylarsine with a very large excess of dibromide of ethylene was digested in sealed tubes at a temperature not exceeding 50° C. Notwithstanding the low temperature, the tubes invariably contained compressed gases; the product of the reaction was treated with water, which extracted

* Proceedings of the Royal Society, "Researches on the Phosphorus-Bases. No. IX. Phosphammonium Compounds," vol. x. p. 608.

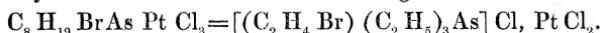
a soluble bromide from the ethylene-compound unacted upon. On evaporation, a beautiful bromide was left, which being copiously soluble in boiling, and sparingly soluble in cold alcohol, could be readily recrystallized from absolute, and even from common alcohol. In water this substance is excessively soluble, and therefore scarcely crystallizable from an aqueous solution.

Analysis, as might have been expected, proved this salt to be the analogue of the bromethylated triethylphosphonium-salt. It contains



The bromide of bromethyl-triethylarsonium, the composition of which is sufficiently established by the analysis of the corresponding platinum-salt, can be obtained in beautiful crystals. Their form was determined by Quintino Sella; it corresponds exactly with that of the corresponding phosphorus-compound.

Platinum-salt.—The solution of the previous salt, converted by treatment with chloride of silver into the corresponding chloride, yields with dichloride of platinum, splendid needles of a double salt, difficultly soluble in cold and even in boiling water, which contain



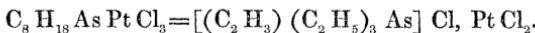
Compounds of Vinyl-triethylarsonium.

The bromide of bromethyl-triethylarsonium, like the corresponding phosphorus-compound, loses its latent bromine under the influence of oxide of silver. If the solution of the bromide be precipitated by an excess of nitrate of silver, one half of the bromine separates as bromide of silver; the clear filtrate mixed with ammonia yields the second half of the bromine in the form of a dense precipitate. Nevertheless the reaction differs from that observed in the phosphorus-series. The bromide of the bromethylated phosphonium, as has been pointed out in a former part of the researches on the phosphorus-bases, is almost invariably converted into an oxethylated body, its transformation into a vinyl-compound being altogether exceptional. The bromide of the bromethylated arsonium, on the other hand, yields as a rule the vinyl-body of the series, the formation of an oxethylated compound taking place only under particular circumstances, in fact so rarely as to leave some doubt regarding the existence of this term of the series.

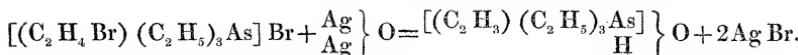
The bromide of bromethylated arsonium, treated with an excess of

* H = 1; O = 16; S = 32; C = 12.

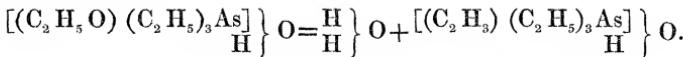
oxide of silver, yields a powerfully alkaline solution, the nature of which was determined by the analysis of the corresponding platinum-salt. Transformed into the chloride and precipitated with dichloride of platinum, this solution yielded beautiful rather soluble octahedra which were found to contain



The analysis of this salt shows that the transformation of the bromoethylated compound ensues according to the following equation,



The idea suggested itself that the vinyl-compound obtained in this reaction might be a secondary product resulting from the decomposition of an oxethylated compound of limited stability formed in the first instance,



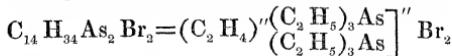
It was with the view of avoiding this decomposition that in one of the operations the digestion was accomplished at the common temperature; the result, however, showed that even in this case the vinyl-compound was obtained.

Nevertheless the oxethylated body appears to exist: under circumstances which were not sufficiently well observed at the time, the action of oxide of silver upon bromide of bromethylated triethylarsonium yielded an octahedral platinum-salt, which on analysis furnished exactly the platinum-percentage of the oxethylated compound.

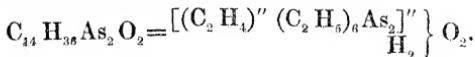
DIARSONIUM SERIES.

Dibromide of Ethylene-hexethyldiarsonium.

The bromide or chloride of the bromethylated arsonium-compound is but slowly acted upon by triethylarsine at 100° C. Two days' digestion at that temperature had produced but a slight impression; at 150° the reaction is accomplished in two hours. The phenomena now to be recorded presented themselves in the succession repeatedly observed in the diphosphonium-series. The dibromide



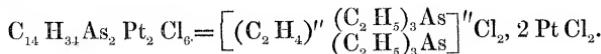
yielded, when debromized, the powerful alkali



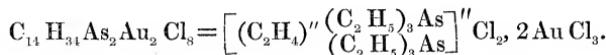
Treated with acids, this alkali produces a series of fine salts, amongst which the di-iodide deserves to be mentioned ; it equals in beauty the corresponding diphosphonium-compound.

I have fixed the composition of the series by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—Pale-yellow crystalline precipitate, similar to the diphosphonium-compound, difficultly soluble in water, soluble in boiling concentrated hydrochloric acid, from which it crystallizes on cooling. It contains



Gold-salt.—The dichloride obtained after separating the platinum in the previous analysis by sulphuretted hydrogen, was precipitated by trichloride of gold ; yellow slightly crystalline precipitate, soluble in hydrochloric acid, from which it crystallizes in golden-coloured plates. The formula of this salt is

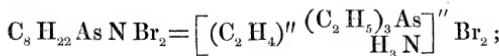


ARSAMMONIUM SERIES.

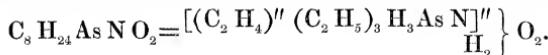
Bromide of bromethylated triethylarsonium, as might have been expected, is capable of fixing ammonia and monamines, giving rise to the formation of a group of compounds not less numerous than the bodies mentioned in the phosphorus-series. I have been satisfied to study the action of ammonia upon the bromide.

Dibromide of Ethylene-triethylarsammonium.

Reaction complete in two hours at 100°. The product contains the dibromide,

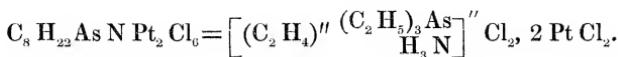


this salt is converted by oxide of silver into the stable caustic base

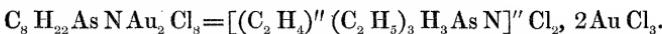


the composition of which was determined by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—Needles, difficultly soluble in boiling water, soluble in concentrated hydrochloric acid, from which well-formed crystals are deposited, containing



Gold-salt.—Yellow compound precipitated from the dichloride obtained in the previous platinum-determination, on addition of trichloride of gold, soluble in hydrochloric acid, deposited from this solution in golden-yellow plates of the composition

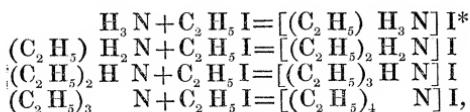


I have also made a few experiments on the action of dibromide of ethylene upon triethylstibine. The reaction is slow, and requires long-continued digestion at temperatures higher than that of boiling water. The tubes invariably contained much gas; and the product of the reaction proved to be a complex mixture of several compounds, many of them secondary, which in no way invited me to a more minute examination of this process. I omit to quote the few platinum- and chlorine-determinations which were made, since they do not admit of a simple interpretation.

IV. "Contributions towards the History of the Monamines."—

No. IV. Separation of the Ethyl-Bases. By A. W. HOFMANN, LL.D., F.R.S. Received November 28, 1860.

The preparation of the ethyl-bases by the action of ammonia upon iodide of ethyl, presents a difficulty which greatly interferes with the general application of this otherwise so convenient method. This difficulty consists in the simultaneous formation of all the four ethyl-bases. The equations



are an ideal representation of the four different phases through which ammonia passes during its transformation into iodide of tetrethylammonium. In practice it is found impossible to carry out this transformation in the several steps indicated by these equations. The first substitution-product, generated as it is in the presence of the agent of substitution, is immediately acted upon again, the second

* $\text{H} = 1$; $\text{O} = 16$; $\text{C} = 12$, &c.